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# DIFFERENCES IN THE ANNIHILATION OF POSITRONS IN OPTICAL ISOMERS

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That asymmetric organic molecules synthesized from a simulated reducing atmosphere are found as a racemic mixture of both L and D optical isomers yet in living nature only one isomer is found has long been realized[1]. Thus the amino acids occurring in natural proteins - save a very few exceptions[2] - belong to the L series. This phenomenon has been the subject of speculation ever since the early work of Pasteur[3], but by far the most exciting of the many hypothesis to be advanced in its explanation[4] is one based on a physical background: the well known "parity non conservation law", proposed by Lee and Yang[5] in 1956 and verified soon after experimentally by Wu et al.[6] According to this view matter is intrinsically asymmetric, because non-conservation of parity would be equivalent to violation of the mirror symmetry of nature. Vester[7] was quick to direct attention to the parallel between the asymmetry of matter and the optical asymmetry of metabolites, but though this idea was expanded on in later work with Ulbricht[8] and by others[9], unequivocal evidence in support of the hypothesis could not be obtained. One of us[10], however, found that when D and L isomers of tyrosine were bombarded for 18 months with $\beta^-$ particles the D isomer decomposed more rapidly. This did indeed suggest that the one-handedness of metabolites is connected with an intrinsic one-handedness of matter, but clearly further experiments were needed[4,11]. With this aim in mind we turned to a study of the annihilation of longitudinally polarized positrons in optical isomers exploiting this technique's great advantage, that it gives information about the interaction process itself rather than about the products of the interaction.

In condensed materials, positrons slow down within $10^{-12}$ s to energies of about 10 eV before annihilation. This may happen in two ways: either a/ by annihilation on free electrons which takes place in $\tau_f = 2.10^{-10}$s; or b/ by formation of positronium /Ps/, i.e. positron-electron atom. In the latter mode the Ps atoms are formed in both singlet /spin=0/ and triplet /spin=1/ states, in the relative proportion of 1:3, but whereas the singlet Ps has a lifetime of $\tau_s = 2.10^{-10}$s, the triplet Ps generally takes longer to annihilate, having a lifetime of $\tau_t = 5\text{-}40.10^{-10}$s, depending on the material. With suitable apparatus it is in fact possible to separate a fast /free positron annihilation + singlet Ps annihilation/ from a slow /triplet Ps annihilation/ component. According to the Ore model[12] the probability of Ps production depends on the

ionization energy and the energy of the first excited state of the molecules of the material.

A number of experiments[13,14,15] have shown that positrons emitted in radioactive decay partly retain their longitudinal polarization during slowing down and Ps formation. Thus Hanna and Preston[13] ascertained that the rate of positron annihilation on magnetized electrons of iron is higher, when external magnetizing field H is parallel to the direction of the positron spins /positron and magnetized electron spin are antiparallel/. Similarly in the annihilation of positrons in plastic material under the influence of an external magnetic field Dick et al.[15] found that the intensity of the slow component /from triplet Ps atoms/ was larger if H was antiparallel to the positron spin.

In the present experiments L-, and D-tryptophan, L-, and D-phenylalanine, L-, and D-tyrosine, and L-, and D-dihydroxy-phenylalanine were investigated. /The companies from which the chemicals were purchased are listed in table 1./ The optical isomers gave identical absorption curve when tested with a Unicam SP 1800 spectrophotometer, and exhibited only one spot on paper chromatograms developed in two different solvent systems /butanol:acetic acid:water 4:1:1; and phenol:water 4:1/. In optical rotatory dispersion and circular dichroism measurements with a JASCO model ORD/UV-5 spectropolarimeter equipped with a circular dichroism attachment they gave mirror symmetrical patterns, as expected. The purity tryptophan and tyrosine was also checked by fluorescence analysis in an OPTON spectrofluorimeter; the relative quantum efficiency was the same for the L and D isomers, which excludes the presence of quenchers such as iron. It should be mentioned that in spite of all efforts some unknown, hardly detectable impurities may interfere with the mechanism of positron annihilation, however, the consistency of the results makes it very unlikely that unknown impurities are responsible for the effect.

To examine positron annihilation the crystalline amino acids were packed around a $^{22}Na$ source of $\sim$0.8 μc activity to a thickness of 6-7 mm and this was placed between two scintillation counters of NE 111 plastic phosphor that were coupled to AVP 56 photomultipliers /see Fig. 1/. Conventional electronic circuits selected coincidences between the 1,28 MeV γ radiation and the 0,51 MeV annihilation radiation, the time delay was measured by a time-to-amplitude converter and multichannel analyser. The number of independent runs for each pair of compounds is given in table 1.

The lifetime spectra for L-, and D-tryptophan presented in Figure 2, display noticable differences. Similar results were obtained with the other three compounds. The computer evaluated data, collected in table 1, show that;

/a/ The intensity of the long-life triplet component diminishes in materials in the order tryptophan > phenylalanine > tyrosine > dihydroxy-phenylalanine.

/b/ The triplet intensity /$I_t$/ in the D amino acids is higher than that in their L isomers;

/c/ The triplet life-time reveals differences for the different pairs.

The experimental findings in this paper are mostly presented from the point of view of origin of optical purity in biological systems, while a detailed analysis of the data will be published elsewhere.

There are clearly significant differences in the annihilation of longitudinally polarized $\beta^+$ particles in optical isomers. The difference in triplet annihilation intensity between L-, and D-amino acids seems to be a basic effect while the differences between the life-time values seen to be of secondary character. This accords well with - and corroborates - the previous experimental findings of Garay[10]. These experiments show that the D-isomers of amino acids favor triplet states in case of forward polarized $\beta^+$ particles and are preferentially destroyed in case of backward polarized $\beta^-$ particles. The electron-electron interaction which is responsible for destroying molecules favors the singlet interaction because of the Pauli principle. It seems very likely, from this evidence, that $\beta$ decay was the cause of an initial asymmetry in the racemic mixtures present on primordial Earth. /It should be kept in mind that about 26 percent of the total radiation energy on the surface of the primordial Earth derived from $\beta$ decay[16]./ This tiny initial asymmetry was probably enough, in the course of chemical and biological evolution, to nudge the system to a highly asymmetric state by one or another of the mechanisms suggested by Wald[17] and others[18].

For the physical interpretation of the effect we rely on the fact[20] that the symmetry properties of optical isomers are compatible with the existence of second rank pseudotensors characterizing the isomers. The correlation tensor $\langle v_\alpha \sigma_\beta \rangle$ between the velocity and the spin of the electrons of the sample is of this type. Therefore those components of the correlation tensor which are allowed by the symmetry may be different from zero. In a solution, for example, the correlation tensor has the form,

$$\langle v_\alpha \sigma_\beta \rangle = K \sigma_{\alpha\beta}$$

where the coefficient K is of different sign in L and D species. In other words, when $K \neq 0$ the electron spins are aligned predominantly parallel to the motion in one of the optical isomers, and antiparallel in the other.

Let us suppose that the probability of positronium formation depends on the relative velocity of the positrons and the electrons. Since the positrons are polarized this assumption immediately leads to the consequence that - when $K \neq 0$ - the relative probabilities of ortho- and para-positronium formation differ for different optical isomers. This difference is indeed observed in the experiment described above.

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Lifetime /$\tau_s$ and $\tau_t$/ and triplet intensity /$I_t$/ data from positron annihilation time spectra. Lifetime values are given in channel numbers. 1 channel = 31 /1/ psec.

| Material | Number of independent runs | L | | | D | | | L/D | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\tau_s$ | $\tau_t$ | $I_t$ | $\tau_s$ | $\tau_t$ | $I_t$ | $\tau_t$ | $I_t$ |
| Phenylalanine /Calbiochem/ | 8 | 10.7/2/ | 28.7/4/ | 11.0/6/ | 10.0/2/ | 27.1/4/ | 13.4/6/ | 1.06/2/ | 0.83/6/ |
| Tyrosine /Sigma Chem. Corp./ | 8 | 10.8/2/ | 38.8/4/ | 4.4/2/ | 10.8/2/ | 38.0/4/ | 4.7/2/ | 1.02/2/ | 0.94/6/ |
| Dihydroxy-phenyl-alanine /Nutritional Biochem. Corp./ | 4 | 9.2/2/ | 33.0/4/ | 1.6/1/ | 9.2/2/ | 36.0/3/ | 2.2/1/ | 0.93/2/ | 0.72/6/ |
| Tryptophan /1/ /Nutritional Biochem. Corp./ | 4 | 10.9/2/ | 34.1/3/ | 12.0/1/ | 10.9/2/ | 30.0/3/ | 18.0/1/ | 1.14/2/ | 0.67/7/ |
| Tryptophan /2/ /Koch-Light. Lab. Ltd./ | 4 | 9.5/3/ | 27.9/4/ | 18.8/10/ | 11.0/2/ | 30.9/3/ | 22.8/10/ | 0.91/2/ | 0.82/5/ |

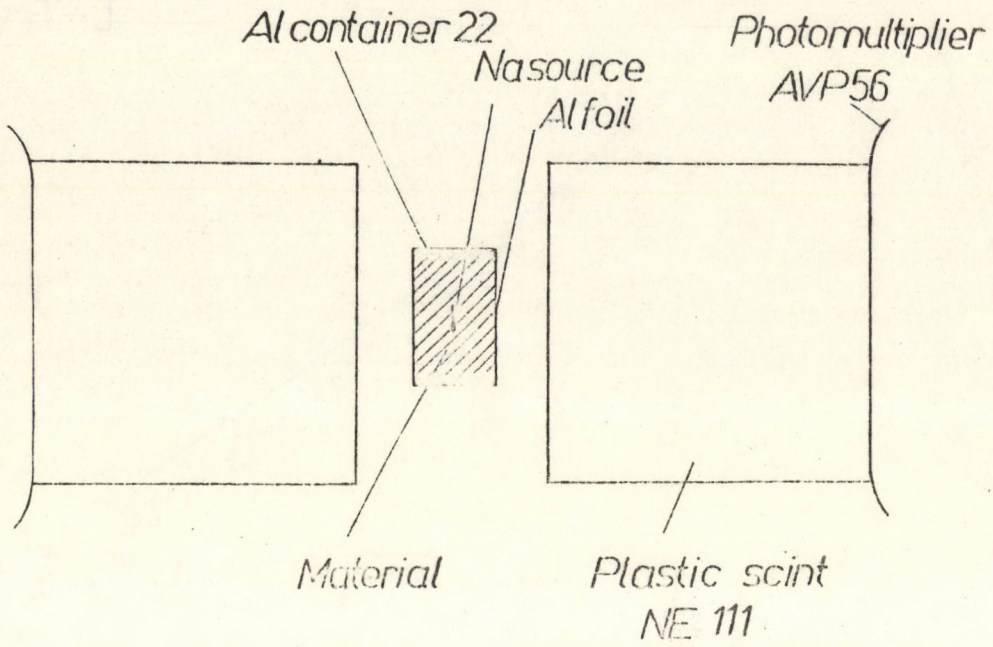



Fig. 1

Arrangement of $^{22}Na$ source, material and plastic scintillators

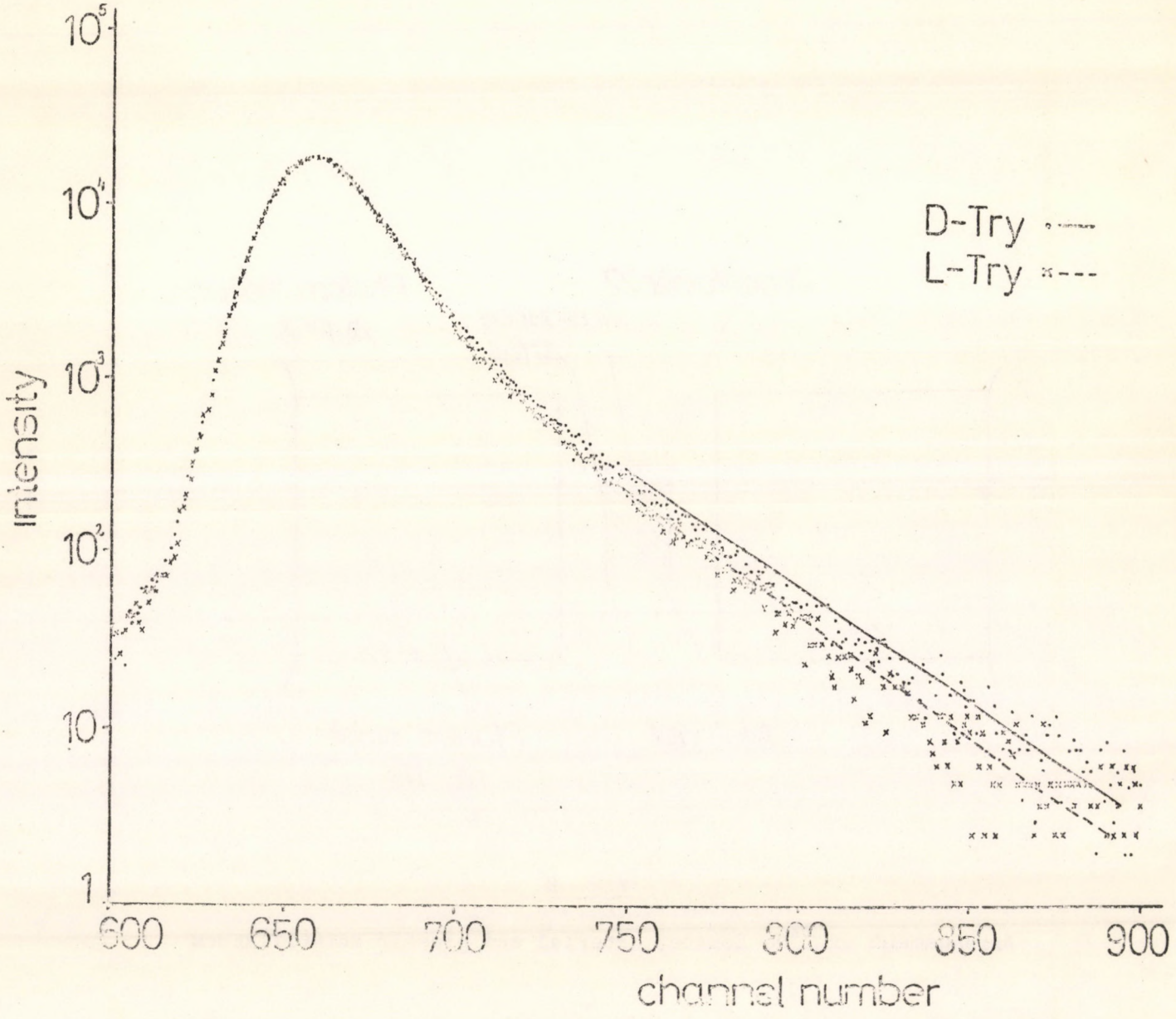
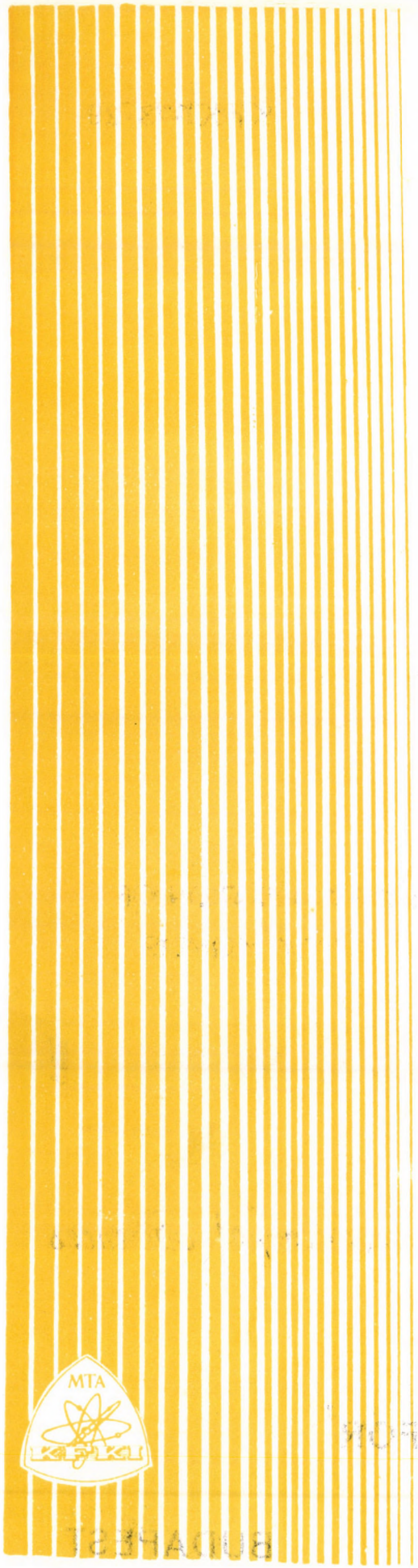



Fig. 2

Positron lifetime spectra in L-, and D-tryptophan /One channel = 31/1/ psec./

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